

## REVIEW ON THE EFFECT OF NANOFILLER ADDITION ON THE TECHNICAL PROPERTIES OF POLYMERS

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### ABSTRACT

*Prime important applications of rubber are such as inner tire liners and fuel hoses which should have excellent gas barrier properties. Much attention has been given by researchers in improving gas barrier properties based on the polymer type or the compounding ingredients. In the variety of commercially available synthetic rubber, Butyl rubber possesses excellent gas barrier properties. Butyl rubber (IIR) is a synthetic rubber produced by copolymerizing isobutylene with small amounts of isoprene. To a small isoprene fraction of butyl rubber, chlorine or bromine is added to form chloro butyl rubber or bromo butyl rubber. This chlorobutyl rubber (CIIR) and bromobutyl rubber (BIIR) has the same property of butyl rubber but they can be cured more rapidly than butyl rubber. The nanoclay used in this study cloisite 30B. Development of butyl rubber nanocomposite has been done in two stages. The first stage is the preparation of chloro butyl nanocomposite (CI-C) by solution mixing and the second stage is the incorporation of chloro butyl nanocomposite in butyl rubber by a vulcanization process. Morphological studies of the butyl rubber nano-composites were analyzed by X-ray diffraction (XRD). TEM used to observe the internal structure of the nanocomposite membranes in an effort to gain further understanding of the permeability properties.*

**KEYWORDS:** Butyl Rubber (IIR), Chlorobutyl Rubber (CIIR) & Nanocomposite (CI-C)

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### INTRODUCTION

In the current situation, nanomaterials are conveyed in polymer lattices in order to enhance the real and warm homes of elastic and plastic composites. Naturally changed montmorillonite organoclay is commonly utilized as nanofillers for preparing nanocomposite with a specific end goal to improve physical, mechanical and fuel hindrance homes. elastic is mixed with naturally adjusted montmorillonite nanoclay (cloisite 15a, cloisite 20a, cloisite 30b), vermiculite, recorite or kaolin with different weight shots (1,2,3,4, et cetera., phr). Be that as it may, upgrade in homes of plastic or elastic nanocomposite depends upon on scattering of nanoclay inside the framework. In a couple of occurrences, reasonable compatabilizer can be utilized for a higher scattering of nanoclay in rubbers and plastics. Mechanical and gas boundary properties of nano composite are advanced because of the higher appropriation of nanoclay in plastics or elastic. Naturally altered elastic nanocomposite locate its utility in inside coating of tires, aeration, and cooling system hoses, oil seals, et cetera. As weight, level of nanoclay will expand gas penetrability of nano composite declines and mechanical property of nanocomposite will increment. A warm strength of the arranged nanocomposite move toward becoming advanced while joining organoclay inelastic. Morphological examinations demonstrated incomplete shedding and in addition agglomeration.

Joined nanocomposite have been also sorted out by utilizing blending polymers with a nanoclay. Expansion of nanoclay permits in enhancing the mechanical and gas barrier properties. Porousness investigates plastic nano composite delights that gas penetrability diminishes while the nanoclay substance will increment inside the nano composite. This assesses article has some expertise in inquire about discoveries on the improvement of elastic and plastic nanocomposite to upgrade mechanical and fuel obstructions living arrangements.

## ABBREVIATION

CIIR - Chlorobutyl rubber, XRD - X Ray Diffraction, TEM - Transmission Electron Microscope, phr - parts per hundred rubber, PP - Polypropylene, EPDM - Ethylene propylene diene rubber, IIR - Isobutylene Isoprene rubber (or) Butyl rubber, PPO - poly(2,6-dimethyl-1,4-phenylene oxide), LDPE - Low density polyethylene, PEMA - Polyethylene grafted maleic anhydride, WAXD - Wide angle x ray diffraction, DSC - Differential scanning calorimetry, LLDPE - Linear low density polyethylene, (PP-g-MA) - Maleic anhydride grafted polypropylene, ED - Electron diffraction, CB - Carbon Black, SBR - Styrene butadiene rubber, ECO - Epichlorohydrin rubber, - Polystyrene, MMT - Montmorillonite, Na - Sodium, VDAC - Vinyl benzidimethyldodecyammonium chloride, VODAC - Vinyl benzyl octadecylidimethyl ammonium chloride, NR - Natural rubber, TGA - Thermo gravimetric analysis, UTM - Universal testing machine, PLA - Polylactide, SMK - Silane modified, PS - Precipitated silica, NBR - Acronitrile butadiene rubber, EVOH - Ethylene vinyl alcohol, XSBR - Carboxylated styrene butadiene rubber, PCL - Poly (caprolactane), poly(2, 6-dimethyl-1, 4-phenylene oxide) (PPO)

## PREPARATION METHODS

This section gives an overview of preparation methods of nanocomposite which has been followed in the literature. Plastic or rubber nanocomposite are prepared by different methods such as

**Solution Mixing** - suitable solvent can be selected to dissolve the polymer observed by means of ultrasonication for even dispersion.

**Melt Intercalation Methods** - polymers and resin or fillers or additives are shear blended at improved temperature.

**Melt Blending** - An improved method of forming a pigmented powder coating composition of the kind wherein the constituents are melt-extruded and the extrude is solidified then ground into a powder is provided.

## NANOCLAY BASED POLYMER NANOCOMPOSITES

Polymer nano composite is a new method of enhancing the properties of polymers and also their utility can be extended to macro scale to nano scale level. Polymernano composite is advancement than conventionally filled particulate nanocomposite. Due to the microstructure of polymer nanocomposite its properties differ from conventional composites materials. The chlorobutyl rubber nanocomposite (CIIR) were prepared using organically modified closite 15A as a filler at different loading (2,5,10 and 20 phr). Dispersion of nanoclay over CIIR matrix will increase the gas barrier property of CIIR nanocomposite. The structure and morphology of the composite were studied using X-ray diffraction (XRD) and transmission electron microscope (TEM). The CIIR nano composite shows major improvement of mechanical properties at a minimum loading of filler. The tensile and tear strength also shows improvement up to 10phr of clay loading. But, after 10phr of clay the properties decrease somewhat because due to a mass of clay[1].

IIR Nanocomposite was prepared by solution mixing method. Here EPDM/Clay nanocomposite film was prepared first and then the IIR further incorporated in the film in the presence and absence of Carbon Black. In this study nanoclay cloisite 20A was used for preparation. The study reveals the nanocomposite prepared using EPDM shows better property than pure IIR nanocomposite. But comparing EPDM nanocomposite with Carbon Black shows higher improvement in its properties than the composites without carbon black. This because of the dual filler in the nanocomposite[2].

Gas barrier properties of butyl rubber/vermiculate nanocomposite coating were studied. Exfoliated vermiculite was applied to PPO with different weight (0, 20 and 30 wt%) percentage in order to form the coating formulation which consists of butyl rubber latex. The permeability of the nanocomposite coatings to various gases was measured and compared to permeation models for nanocomposite. In high weight percentage of vermiculite gas permeability and time lag data of the nanocomposite materials were decreased. TEM and SEM were used to observe the internal structure of the nanocomposite membranes for a better understanding of the permeability properties. Independent gas absorption isotherm experiments for CO<sub>2</sub> were found to be larger in nanocomposite than in butyl rubber[3].

The IIR /clay nanocomposite was prepared by two steps using butyl alcohol as swelling agent followed by shear mixing to produce IIR/swollen organic modified clay compounds. The increase in the amount of clay increases the gas barrier properties and mechanical properties of IIR/Clay nanocomposite. The swollen organoclay nanocomposite shows superior in tensile strength and air tightness when compared to the nanocomposite made by solution intercalation and traditional melts intercalation method. The nanocomposite IIR/clay can be used in rubber products which require high gas barrier properties such as tire inner-tube and inner-liner[4].

Butyl rubber nanocomposite was prepared by solution (or) melt intercalation method. Clay dispersion of prepared nanocomposite was studied by using TEM and XRD. Exfoliation and intercalation of clay layers were observed from TEM images. An aspect ratio of nanocomposite prepared by solution intercalation is larger than that of melt intercalation. XRD images revealed that basal spacing of clay has been increased from 2.2nm (organically modified clay) to 4.2 nm (nanocomposite). The prepared IIR/clay nanocomposite shows outstanding performance for mechanical and gas barrier properties. The IIR/clay nanocomposite prepared by the solution intercalation method shows superior performance than the melt intercalation prepared nanocomposite [5].

IIR/ clay Nano composite was prepared by melt intercalation with maleic anhydride grafted IIR (Ma-g-IIR) and organophillic clay. When comparing these two nanocomposites the IIR / clay exhibit good gas barrier properties than (Ma-g-IIR) composite and also the IIR / clay nanocomposite shows 2.5 times greater gas barrier property than maleic anhydride grafted IIR nanocomposite when 15 phr clay added to the IIR/clay nanocomposite [6].

Nitrile Butadiene rubber nanocomposite was prepared and its characters were studied. Epoxidized natural rubber was used as compatabilizer. In this study the epoxidized natural rubber/Cloisite 20A nanocomposite film was prepared using solution mixing method and then the nitrile butadiene rubber was incorporated in the film using an open two roll mill. The characteristic and mechanical studies reveal that the nitrile butadiene rubber with compatabilizer shows improvement in its properties than the nanocomposite without compatabilizer [7].

NBR / organo- montmorillonite nanocomposite was prepared by melt intercalation process. Using oscillating-disk rheometer, water-vapour transmission and transmission electron microscopy (TEM) characteristics of

the nanocomposite characteristics were evaluated. The result revealed the clay content plays the major role in the permeability property of nanocomposite[8].

The compound nanocomposite ready victimization hydrophobic polymers are extremely tough while not victimization compatibilizer. Here hydrocarbon rubber/cloisite clay nanocomposite was ready with success while not victimization compatibilizer. The nanocomposite was ready by softening combining technique. Here cloisite 20A and 15A were used for nanocomposite preparation. The cloisite 20A and 15A were same, however the sole distinction was modifier concentration. The preparation was distributed in Haake internal mixture, followed by the addition of sulphur in an exceedingly 2 roll mill. The hydrocarbon rubber/ cloisite 20A show higher improvement in mechanical properties. it's two occasions higher than pure hydrocarbon rubber with abrasion resistance [9]

Nanocomposite was prepared by using acrylonitrile–butadiene rubber (NBR), vinyl groups containing organically modified montmorillonite and additives, such as zinc oxide, stearic acid, and sulphur. NBR nanocomposite was prepared by a mixer and hot press process simultaneously controlling vulcanization. XRD images of the nanocomposite describe that exfoliated and intercalated structures are formed. The NBR nanocomposite exhibit much higher mechanical properties as well as gas barrier properties when compared to pure NBR and NBR without vinyl groups. XRD and TEM images show that intercalation and exfoliation structures coexist in the nanocomposite [10].

The NR/ rectorite nanocomposite was prepared by coagulating NR latex and rectorite aqueous suspension. The TEM and XRD were employed to characterize the microstructure of the nanocomposite. The result shows that the higher glass transition temperature of the nanocomposite. The gas barrier property improved remarkably in NR/ rectoritenano composite due to the nano scale size of rectorite introduced over the NR surface [15].

The natural rubber nanocomposite was prepared using organoclay and silica as a filler. The organoclay was used at three different proportions (2, 4 and 8phr). The nanocomposite was prepared in an open two role mill. The morphological and characteristics study reveals the nanocomposite made of organoclay as filler shows better results than the silica as a filler. The nano composite with 4phr of organoclay shows better mechanical behavior which is obtained by 50phr of silica. The organoclay reduces 12.5 times the filler content without affecting other properties [11].

Natural rubber-styrene butadiene rubber nanocomposite was prepared using cloisite 15A at low weight percentages (1wt%, 2wt%, and 3wt %). The preparation was carried out in two role mill. When observing the clay filled rubber composite its structure was exfoliated up to 2wt% of clay and intercalated structure at 3wt% of nanoclay. The nanocomposite with 2wt% of the clay shows an increase in tear strength, but at 3wt% of clay it decreases. This is due to the agglomeration of clay. The improvement of hardness and modulus in the nanocomposite was particularly at 2wt% of clay [12].

Polybutadiene Rubber Nanocomposite was prepared with different organoclay (Cloisite10A, 15A, 20A, 30B). The vulcanization behavior and mechanical properties of polybutadiene rubber were studied for different modifier concentrations of Organoclay. The nanocomposite was prepared in Haake internal mixer followed by the addition of sulphur and other additives to the nanocomposite in a two-roll mill. The scorch time and cure of polybutadiene rubber/ nanocomposite were much reduced than the polybutadiene rubber. This due to the ammonium in the organoclay. The organoclay with higher ammonium modifier concentration will show higher torque difference and faster vulcanization

rate to the polybutadiene rubber/ nanocomposite. Among all polybutadiene / organoclaynanocomposite the nanocomposite made of cloisite 15A shows higher improvement in mechanical properties [13].

The nano and micro composites were prepared from natural rubber, carboxylated styrene butadiene rubber and with their bends in the ratio 70:30 natural rubber/carboxylated styrene butadiene rubber. The sodium bentonite and fluorohectorite used as nano fillers for preparation of nanocomposite. Silica and clay used as micro fillers for preparation of micro composites. The XRD and TEM used to study the filler dispersion over rubber matrix. For investigation of gas barrier property of nanocomposite positron annihilation lifetime spectroscopy was used. The nano filled composite exhibits high gas barrier property than the micro composites due to the platelet-like morphology was observed in the prepared nanocomposite [14].

SBR/Recorite nanocomposite was prepared by co-coagulation of SBR latex and rectorite. The dispersion of rectorite over SBR matrix was studied using TEM. The XRD results reveal that the nanocomposite prepared by this method is neither exfoliated nor intercalated. It shows better gas barrier and mechanical properties. Rectorite acts the best filler for nanocomposite [15].

The nanocomposite SBR/clay prepared by mechanical mixing in a pretender mixer and 2-roll mill. The SBR/clay nanocomposite prepared for five types of clay such as unmodified sodium montmorillonite clay, MMT modified with octadecylamine, zwitterionic surfactant modified MMT, and polymerizable cationic surfactant modified MMT and vinylbenzloctadecylidimethy / ammonium chloride. The clay ,rubber nanocomposite was studied by XRD and the result reveals that the mechanical and gas barrier property of composite depends on the amount of clay over pure rubber. SBR nanocomposite with 30 phr with octadecylamine modified MMT observed excess tensile strength with 18MPa. Among those five rubbers/ clay nanocomposite the oxygen permeability of SBR/ vinylbenzloctadecylidimethy / ammonium chloride - MMT is reduced up to 60% [16].

The recorite clay layered with silicate and styrene-butadiene rubber the nanocomposite prepared. When comparing SBR/ recoritenanocomposite with SBR/Recorite shows great improvement in their properties. The gas barrier and mechanical properties of SBR/Recorite clay were great because of its platelet-like morphology [17].

A Series of highly filled natural rubber composites prepared with silane modified kaolin (SMK), precipitated silica (PS) and their mixed- compound addition were prepared by melt mixing. The kaolonite was used as filler for the preparation of Rubbber/Clay nanocomposite and arranged in parallel orientation. The TEM images show a parallel orientation of finely dispersed kaolonite over the surface of rubber matrix . The results revealed excellent gas barrier and mechanical properties for highly filled NR/ SMK Comparing NR/ PS & NR / SMK &PS [18].

Silicon rubber is better for thermal insulation in rocket motors because of its heat resisting, excellent elastic and restoring force. But silicon rubber has poor adhesion property so to overcome this amine groups are added to the silicon rubber. The addition of carbon black will enhances the adhesion property of silicon rubber. Here the amine group is added to the silicon rubber by co-polymerization process. The results revealed that the silicon rubber/ Cloisite 30B shows better improvement of adhesion property than that of the carbon black [19].

The nanocomposite EPDM/ organoclay prepared by melt blending. The compatibilizer used in this preparation maleic anhydride modified EPDM oligomer (EPDM-MA). XRD is used for the evaluation of clay dispersion on nancomposite. The EPDM / organoclaynanocomposite evaluation shows that their improvement in physical and

mechanical properties better than the EPDM without clay. EPDM/ organ clay can be prepared by the straight forward method, it is an alternative for melt blending. The nanocomposite prepared by these two methods shows similar in their properties, but the straight forward method is generally used in industries due to their low cost. Increase in clay content increases the tensile strength, tensile modules and gas barrier properties of nanocomposite [20].

The hybrid nanocomposite EPDM / organoclay were prepared by melt compounding process. The structure of the nanocomposite was studied using x-ray diffraction and transmission electron microscopy. The tensile and tear strength of the hybrid nanocomposite increased remarkably. The oxygen permeability of the hybrid nanocomposite reduced drastically [21].

PP/EPDM rubber is blended with montmorillonite organoclay to form nanocomposite by using melt blending. The PP/EPDM nanocomposite was prepared in the composition of PP/EPDM in 50:50ratio. For better diffusion of nanoclay over PP/EPDM blend compatibilizer was used. Here anti-oxidant acts as a compatibilizer. XRD was used for calculating the diffusion of nanoclay over PP/EPDM rubber matrix. The calculation revealed at low clay content the diffusion of nanoclay was good in the prepared nanocomposite. The addition of 1.5 volume % of organoclay increases the barrier property of oxygen and carbon dioxide in PP/EPDM blend drastically. Organoclay plays a major role in the improvement of barrier property [22].

Melt-mix method is involved in the preparation of Low density polyethylene (LDPE)/clay nanocomposite. PEMA is used as a compatabilizer. The melt mixing carried is out in twin screw extrude. The nanocomposite was studied using Wide-Angle X-ray Diffraction (WAXD) and differential scanning calorimetry (DSC). The result revealed that the increase in PEMA shows an increase in the clay dispersion over nanocomposite. This also decreases the degree of crystallinity. Oxygen permeability test of the LPDE/ clay nanocomposite revealed that the decrease of oxygen permeability of 24% when the clay content increases by 7wt% [23].

The nanocomposite LLDPE/clay is prepared by melt processing technique. Organoclay with 5 phr is mixed with LLDPE. The clay and oxidized polyethylene show increase in physical performance of the nanocomposite. The oxygen permeability value is higher in nanocomposite made by conventional compatiblizer. But composite made of oxidized polyethylene as compatibilizer has lower oxygen permeability value [24].

Ethylene vinyl acetate, low- density polyethylene and high density polyethylene nanocomposities were prepared by adding organically modified screw extruder. When comparing these three nanocomposities ethylene vinyl acetate/clay nano composite shows an increase in the barrier and mechanical properties. The study reveals the property increased with increase in clay loading. The oxygen barrier and mechanical property of ethylene vinyl acetate/clay nano composite was doubled when 5wt% of clay added to the nanocomposite [25].

Nanocomposite is prepared by encapsulating organoclay in epoxy, latex particle through phase inversion emulsification. At 1-2 wt. % of clay loading the size of encapsulated clay particles into water borne epoxy increased by 5 to 10 times. The XRD and TEM show the intercalation and exfoliation of clay platelets in the epoxy matrix. The organoclay loading increases gradually the oxygen barrier property. The oxygen barrier property increases 3% when 2wt% of clay is added in epoxy/closite30B nanocomposite. But comparing to epoxy/modified clay nanocomposite it shows greater oxygen barrier property for the same 2wt% of clay than the epoxy /cloister 30B nanocomposite for the same 2wt%.

The study of water bone epoxy-clay nanocomposite reveals that the kind of organoclay plays a major role in the gas barrier property. Short alkyl ammonium salt ,modified natural clay has the great oxygen barrier property [26].

### CARBON BASED POLYMER NANOCOMPOSITES

Under different content of carbon black the EPDM elastomer characteristics were studied. The dispersion of fillers has an influence on the improvement of properties of EPDM the commonly used carbon black as the filler for EPDM. At a low manufacturing cost the carbon black filled EPDM elastomer rubber shows good physical and mechanical property. The increase in CB content in EPDM elastomer obviously reduces the oxygen content when comparing the EPDM without a CB shows increase in oxygen content [27].

The shockwave propagation method used for the synthesis of carbon nanoparticles and twin screw co-rotating extruder was used for the dispersing carbon nanoparticles over the surface of isotactic-polypropylene. By increasing in filler content of nanocomposite the air permeability decreases gradually [28].

The NR / nano carbon black composite was prepared by two-roll mill at different loadings of 10phr, 20phr & 30phr. The NR / clay composite was prepared for different leading by the emulsion compounding method. The NR / clay / carbon black at same filler loading exhibits great mechanical properties without any difference. The NR / carbon black composite exhibit good gas barrier properties than the NR / clay nanocomposite [29].

### GRAPHITE BASED POLYMER NANOCOMPOSITES

To disperse the graphite nanosheets into the polymer matrix for preparing elastomer/graphite nanocomposite facile latex approach was used. The study of nitrile-butadiene rubber/graphite nanocomposite under transmission electron microscopy and X-ray diffraction reveals the composite has good exfoliated and the intercalated structure of NBR/graphite nanocomposite. The gas barrier property and the mechanical property were improved drastically in NBR/graphite nanocomposite [30].

### CONCLUSIONS

The review explores the summary of preparation and characterization of rubber or plastic nanocomposite is summarized as follows. Nanocomposites are ready by answer mix followed by softening mix. The characterization of ready nanocomposite was studied by mistreatment XRD, TEM, TGA, FTIR, tensile, permeableness take a look at then on. From the review it's tested that uniform dispersion of nanoclay ends up in improvement of mechanical, thermal and gas barrier properties. Compatibilizer act as a phase for nanoclay within the matrix. A lot of over compared to any or all kinds of nanoclay, organically changed nanoclay composites shows higher results. The considerably addition of nanoclay shows outstanding changes in improvement of gas barrier properties.

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